Reversible Dimerization of (+)-Myrmicarin 215B

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Supporting Information

Contents:

General Procedures. All reactions were performed in dry 5 mm o.d. NMR tubes for *in situ* reaction monitoring. The NMR tubes were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60 Å pore size, 40-63 μm, 4-6% H_2O content, Zeochem).[1] Where necessary (noted), silica gel was neutralized by treatment of the silica gel prior to chromatography with the eluent containing 2.5% triethylamine. Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel or alumina gel impregnated with a fluorescent indicator (254 nm). Where necessary (noted), silica gel plates were neutralized by treatment with a solution of 2.5% triethylamine in ethyl acetate followed by heating on a hot plate (~250 °C). Thin layer chromatography plates were visualized by exposure to ultraviolet light and/or by exposure to an aqueous solution of ceric ammonium molybdate (CAM) followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~20 Torr at 25–35 °C unless otherwise indicated.

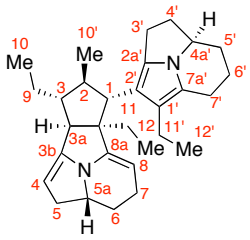
Materials. Commercial reagents and solvents were used as received. Dichloromethane-d_2 solutions were deoxygenated by alternate freeze (liquid nitrogen)/evacuation/argon-flush/thaw cycles (FPT, three iterations) and neutralized by stirring over potassium carbonate.

Instrumentation. Solutions were irradiated using a Hanovia 450-watt medium pressure mercury lamp at a distance of 7.0 cm from the lamp and a temperature of 23 ºC. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian inverse probe 500 INOVA spectrometer or a Bruker inverse probe 600 Avance spectrometer. Chemical shifts are recorded in parts per million

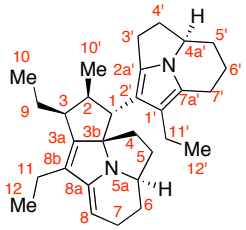
[1] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

on the δ scale and are referenced from the residual protium in the NMR solvent (C_6D_5H: δ7.16). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian 500 INOVA spectrometer. Chemical shifts are recorded in parts per million on the δ scale and are referenced from the carbon resonances of the solvent (C_6D_6: δ 128.4). Infrared data were obtained with a Perkin-Elmer 2000 FT-IR and are reported as follows: [frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad), assignment]. We are grateful to Dr. Li Li for obtaining the mass spectroscopic data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High-resolution mass spectra (HRMS) were recorded on a Bruker APEX 4.7 Tesler FTMS spectrometer using electronspray ion source (ESI).

Positional Numbering System. For direct comparison, the numbering scheme used for dimeric compounds is consistent with that used by Schröder and coworkers in the isolation paper for myrmicarin 430A[2] and that used previously by us for isomyrmicarin 430A.[3]



Myrmicarin 430A
(**M430A**)



Isomyrmicarin 430A
(**isoM430A**)

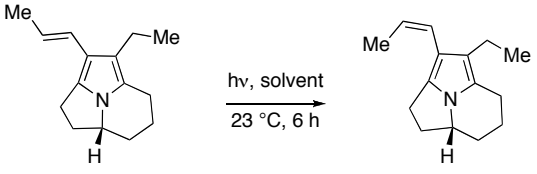
[2] Schröder, F.; Sinnwell, V.; Baumann, H.; Kaib, M. *Chem. Commun.* **1996**, *18*, 2139–2140.
[3] Ondrus, A. E.; Movassaghi, M. *Tetrahedron* **2005**, *62*, 5287–5297.

Additional Notes.

*A) Supplementary notes on photochemical irradiation of **M215B**:*

- Irradiation of a solution of **M215B** in benzene, acetonitrile, or hexanes using a 450-watt medium-pressure mercury lamp effected partial isomerization to the **M215A** olefin isomer (Table S1).
- Irradiation of a methanolic solution of **M215B** provided both **M215A** and methanol adduct **S1** as a 1:1 mixture of diastereomers (Scheme S1).[4]
- **M215A** was not detected during irradiation of **M215B** in dichloromethane-d_2.

Table S1. Photochemical activation of **M215B**.[a]

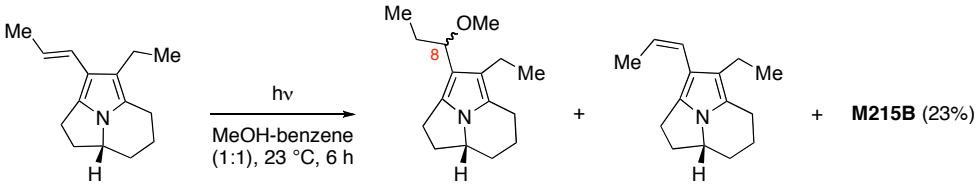


M215B **M215A**

solvent	product ratio M215A : M215B	isolated yield (%)[a]
CH_3CN	16 : 84	76
C_6H_6	33 : 67	93
hexanes	19 : 81	60

[a] Combined isolated yield; ratio determined by ^{1}H NMR.

Scheme S1.



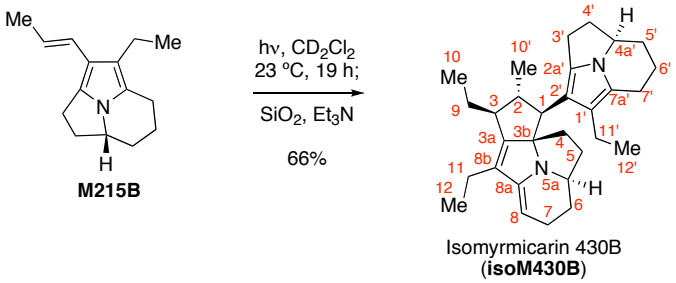
M215B **S1** (41%, 1:1 dr) **M215A** (23%)

*B) Supplementary notes on HCl-induced dimerization of **M215B**:*

Generation of HCl:

- Treatment of a dichloromethane-d_2 solution of **M215B** with hydrochloric acid (1.40 equiv) in the dark for 20 hours followed by filtration of the reaction mixture through triethylamine-pretreated silica gel provided **isoM430B** as the sole product in 30% yield.
- Irradiation of a dichloromethane-d_2 solution of **M215B** containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2.60 equiv) for 10 hours returned exclusively **M215B**.
- Irradiation of a dichloromethane-d_2 solution of **M215B** containing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.10 equiv) for 6 hours returned exclusively **M215B**.
- Reactions conducted in dichloromethane provided results identical to those conducted in dichloromethane-d_2, indicating that photochemical generation of HCl versus DCl did not influence the outcome or rate of these transformations to an observable extent.

[4] For examples of nucleophile addition to alkenes under photochemical irradiation, see: (a) Moran, J.; Cebrowski, P. H.; Beauchemin, A. R. *J. Org. Chem*. **2008**, *73*, 1004–1007. (b) Shim, S. C.; Kim, D. S.; Yoo, D. J.; Wada, T.; Inoue, Y. *J. Org. Chem*. **2002**, *67*, 5718–5726. (c) Kropp, Paul J. *J. Am. Chem. Soc.* **1966**, *88*, 4091-–4092. (d) Marshall, J. A.; Carroll, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4092–4093. For a discussion of photochemically induced reactions of cycloalkenes, see: Marshall, J. A. *Science* **1970**, *170*, 137–141.



Isomyrmicarin 430B (isoM430B):

A sample of **M215B** (29.5 mg, 137 μmol, 1 equiv) in neutralized, degassed dichloromethane-d_2 was sealed in an NMR tube under an argon atmosphere and was irradiated at 23 ºC for 19 h. The resulting deep brown reaction mixture was filtered through silica gel neutralized with triethylamine (2.5% Et_3N and 2.5% EtOAc in hexanes, diam. 1.5 cm, ht. 13 cm) to afford **isoM430B** (19.4 mg, 66%) as a pale yellow oil. Isolated samples of **isoM430B** undergo complete decomposition after approximately four hours in degassed benezene-d_6 at 20 ºC.

Samples for spectroscopic analysis were prepared immediately and high quality data was acquired within two hours of isolation. Complete assignment was possible with the aid of additional information from gCOSY, HSQC, gHMBC, and NOESY.

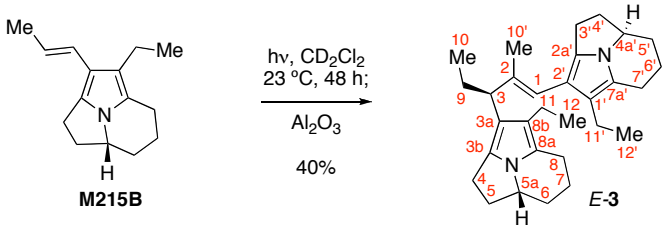
^{1}H NMR (500 MHz, C_6D_6, 20 ˚C): 4.72 (dd, J = 7.3, 3.2 Hz, 1H, C8-H), 3.45 (dq, J = 9.6, 6.4 Hz, 1H, C5a–H), 3.22 (tdd, J = 10.5, 5.0, 3.6 Hz, 1H, C4a'–H), 3.09 (dq, J = 14.5, 7.3 Hz, 1H, C11'–H), 2.92 (d, J = 11.7 Hz, 1H, C1–H), 2.69 (dd, J = 14.3, 7.8 Hz, 1H, C3'–H_t), 2.54–2.64 (m, 3H, C3'–H_c, C11'–H', C7'–H_c), 2.42 (ddd, J = 15.4, 13.1, 8.1 Hz, 1H, C7'–H_t), 2.18–2.30 (m, 5H, C11–H, C2–H, C7–H_t, C3–H, C11–H'), 2.08–2.15 (m, 1H, C7–H_c), 2.02 (dt, J = 11.5, 5.7 Hz, 1H, C4'–H_c), 1.86 (dt, J = 11.4, 5.6 Hz, 1H, C4–H_c), 1.78–1.86 (m, 1H, C6–H_c), 1.48–1.68 (m, 8H, C9–H, C6'–H_t, C5–H_c, C9–H', C4'–H_t, C5'–H_c, C4–H_t, C5–H_t), 1.26–1.39 (m, 1H, C6'–H_c), 1.24 (t, J = 7.2 Hz, 3H, C12'–H), 1.22 (d, J = 6.8 Hz, 3H, C10'–H), 1.17 (t, J = 7.6 Hz, 3H, C12–H), 1.00–1.12 (m, 1H, C6–H_t), 1.03 (t, J = 7.6 Hz, 3H, C10–H), 0.89 (br q, J = 13.1 Hz, 1H, C5'–H_t).

^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 155.7 (C8a), 152.7 (C3a), 132.4 (C8b), 126.7 (C2a'), 124.4 (C1'), 118.6 (C7a'), 112.3 (C2'), 89.1 (C8), 88.2 (C3b), 56.3 (C5a), 55.1 (C4a'), 54.1 (C1), 48.4 (C2), 45.2 (C3), 37.8 (C4'), 36.1 (C5), 31.8 (C4), 30.5 (C5'), 30.4 (C6), 29.5 (C9), 27.5 (C3'), 23.2 (C6'), 22.6 (C7), 20.9 (C7'), 20.2 (C10'), 19.4 (C11), 18.7 (C11'), 17.4 (C12'), 14.4 (C12), 13.5 (C10).

FTIR (thin film) cm^{-1}: 2929 (s), 1737 (w), 1642 (w), 1454 (m), 1372 (w), 1320 (w), 1167 (w).

HRMS (ESI): calc'd for $C_{30}H_{43}N_2$ $[M+H]^+$: 431.3421,
found: 431.3413.

TLC (2.5% Et_3N in [2.5% EtOAc in hexanes], Et_3N neutralized silica gel), *Rf*: 0.40 (UV, CAM).



Hexacyclic Alkene 3:

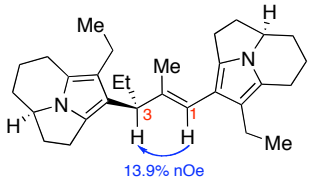
A solution of **M215B** (10.3 mg, 50.2 μmol, 1 equiv) in neutralized, degassed dichloromethane -d_2 was sealed in an NMR tube under an argon atmosphere and was irradiated at 23 ºC for 48 h. The resulting deep brown reaction mixture was filtered through neutral alumina gel (10% Et_2O in pentane, diam. 1.5 cm, ht. 8.5 cm) to afford *E*-**3** (4.3 mg, 40%) as a white solid.

Highest quality spectra were obtained by immediate use of samples and complete assignment was possible with the aid of additional information from gCOSY, HSQC, and gHMBC.

Data for *E*-**3**:

^{1}H NMR (500 MHz, C_6D_6, 20 ˚C): 6.65 (s, 1H, C1–H), 3.60 (dd, *J* = 8.5, 6.8 Hz, 1H, C3–H), 3.26–3.34 (m, 2H, C4a'–H, C5a–H), 2.54–2.79 (m, 9H, C4–H_c, C4–H_t, C11'–H, C11'–H', C11–H, C11–H', C7'–H_c, C8–H_c, C3'–H_c), 2.38–2.49 (m, 3H, C3'–H_t, C7'–H_t, C8–H_t), 2.06–2.14 (m, 1H, C9–H), 1.98–2.04 (m, 2H, C5–H_c, C9–H'), 1.94 (s, 3H, C10'–H), 1.86–1.91 (m, 1H, C4'–H_c), 1.58–1.69 (m, 3H, C6'–H_t, C7–H_t, C5–H_t), 1.42–1.58 (m, 3H, C5'–H_c, C6–H_c, C4'–H_t), 1.26–1.40 (m, 2H, C6'–H_c, C7–H_c), 1.36 (t, *J* = 7.5 Hz, 3H, C12–H *or* C12'–H), 1.35 (t, *J* = 7.5 Hz, 3H, C12–H *or* C12'–H), 1.18 (t, *J* = 7.3 Hz, 3H, C10–H), 0.88 (br q, *J* = 11.5 Hz, 1H, C6–H_t), 0.80 (br q, *J* 12.2 Hz, 1H, C5'–H_t).

nOe data (500 MHz, C_6D_6, 20 ˚C):

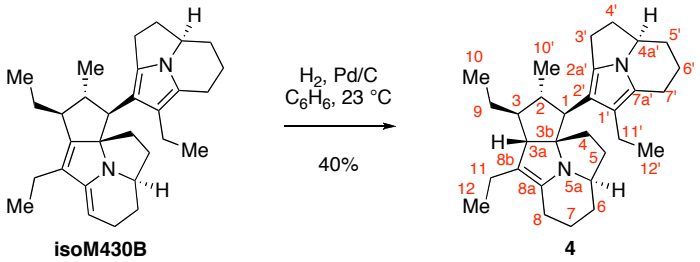


^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 137.6 (C2), 128.9 (C2a'), 126.9 (C3b), 122.4 (C8b), 122.3 (C1'), 119.1 (C1), 118.9 (C8a), 118.4 (C7a'), 117.0 (C3a), 114.0 (C2'), 55.5 (C4a' *or* C5a), 55.0 (C4a' *or* C5a), 49.5 (C3), 37.8 (C4'), 37.4 (C5), 30.5 (C5' *or* C6), 30.4 (C5' *or* C6), 27.5 (C3'), 27.2 (C4), 26.7 (C9), 23.2 (C6' *or* C7), 23.0 (C6' *or* C7), 21.1 (C7' *or* C8), 21.0 (C7' *or* C8), 19.6 (C11'), 19.3 (C11), 17.0 (C12 *or* C12'), 16.9 (C12 *or* C12'), 16.0 (C10'), 13.9 (C10).

FTIR (thin film) cm^{-1}: 2926 (s), 1699 (m), 1457 (m), 1378 (w), 1262 (w), 1089 (w).

HRMS (ESI): calc'd for $C_{30}H_{43}N_2$ $[M+H]^+$: 431.3421,
found: 431.3413.

TLC (15% EtOAc in hexanes, neutral alumina gel), *Rf*: 0.59 (UV, CAM).



Heptacyclic Enamine 4:

A suspension of **isoM430B** (31.3 mg, 72.7 μmol, 1 equiv) and Pd (10% on activated carbon, 62.6 mg, 200 wt%) in benzene (2.50 mL) was stirred vigorously under a dihydrogen atmosphere (1 atm) at 23 ºC for 25 min. The reaction mixture was filtered through a plug of celite (EtOAc, diam. 0.6 cm, ht. 5.5 cm) and the reaction flask and plug were rinsed with additional portions of EtOAc (3 × 3 mL). The clear yellow filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 2.5% Et_3N, 1.5% EtOAc, and 1.5% CH_2Cl_2 in hexanes, diam. 1.5 cm, ht. 6 cm) to give **4** (12.7 mg, 40%) as a yellow oil. Samples of **4** in degassed benzene-d_6 undergo complete decomposition within four days at 20 ºC.

High quality spectra were acquired within 24 hours of isolation. Complete assignment was possible with the aid of additional information from gCOSY, gHSQC, gHMBC, and gNOESY

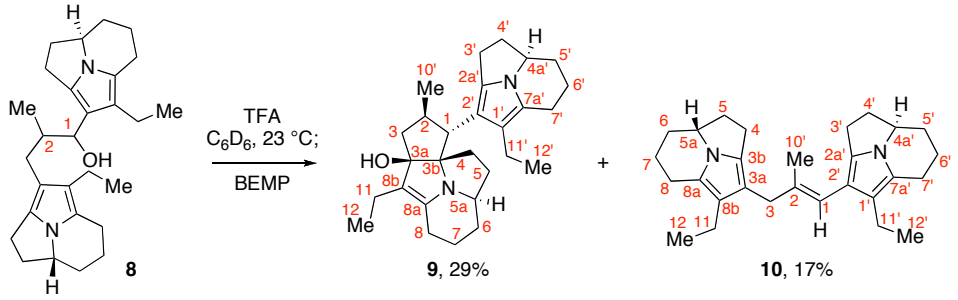
^{1}H NMR (600 MHz, C_6D_6, 20 ˚C): 3.31–3.37 (m, 1H, C4a'–H), 3.27 (d, J = 12.4 Hz, 1H, C1–H), 3.15 (m, 1H, C5a–H), 3.08 (dq, J = 14.4, 7.4 Hz, 1H, C11'–H), 2.96 (d, J = 8.9 Hz, 1H, C3a–H), 2.57–2.70 (m, 4H, C11'–H', C7'–H_c, C3'–H_c, C3'–H_t), 2.51 (ddd, J = 19.5, 15.3, 10.3 Hz, 1H, C7'–H_t), 2.34 (dt, J = 13.5, 4.5 Hz, 1H, C8–H_t), 2.19–2.28 (m, 2H, C11–H, C11–H'), 1.94–2.12 (m, 3H, C4'–H_c, C4–H_c, C8–H_c), 1.70–1.91 (m, 7H, C6–H_c, C2–H, C4'–H_t, C6'–H_t, C9–H, C9–H'), 1.50–1.70 (m, 3H, C3–H, C5'–H_c, C5–H_t), 1.33–1.46 (m, 4H, C6–H_t, C7–H_c, C4–H_t, C6'–H_c), 1.40 (t, J = 7.2 Hz, 3H, C12'–H), 1.19–1.30 (m, 1H, C7–H_t), 1.05–1.16 (m, 1H, C5–H_c), 1.15 (d, J = 6.6 Hz, 3H, C10'–H), 1.14 (t, J = 7.5 Hz, 3H, C12–H), 1.09 (t, J = 7.5 Hz, 3H, C10–H), 0.93 (br q, J = 12.2 Hz, 1H, C5'–H_t).

^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 139.3 (C8a), 127.8 (C2a'), 123.6 (C1'), 118.2 (C7a'), 115.7 (C8b), 115.0 (C2'), 82.5 (C3b), 63.4 (C3a), 59.9 (C5a), 57.0 (C1), 55.2 (C4a'), 54.3 (C3), 44.2 (C2), 38.0 (C4'), 35.8 (C4), 30.3 (C5'), 29.4 (C5), 27.4 (C6), 26.9 (C3'), 25.3 (C9), 24.5 (C8), 23.2 (C6'), 21.1 (C7'), 21.0 (C7), 19.9 (C11), 19.0 (C11'), 18.2 (C10'), 17.6 (C12'), 14.7 (C12), 10.9 (C10).

FTIR (thin film) cm^{-1}: 2919 (s), 1660 (m), 1456 (m), 1265 (w), 1167 (w), 737 (m).

HRMS (ESI): calc'd for $C_{30}H_{45}N_2$ $[M+H]^+$: 433.3577,
found: 433.3593.

TLC (2.5% Et_3N in [2.5% EtOAc in hexanes], Et_3N neutralized silica gel), *Rf*: 0.42 (UV, CAM).



Heptacyclic Alcohol 9 and Hexacyclic Alkene 10:

A solution of alcohol **8**[5] (11.4 mg, 27.0 μmol, 1 equiv) in benzene-d_6 (810 μL) at 23 ºC was degassed thoroughly by passage of a stream of argon. A solution of trifluoroacetic acid (TFA, 2.08 μL, 27.0 μmol, 1.00 equiv) in benzene-d_6 (40.0 μL) was added in four equal portions at three minute intervals. After 5 h, the NMR tube was moved into a glovebox and the bright yellow reaction mixture was transferred to a flask containing 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (BEMP, 50.0 mg, 111 μmol, 4.10 equiv) under dinitrogen atmosphere. The resulting suspension was stirred vigorously for 30 min and the reaction mixture was filtered through a plug of cotton. The filtrate was removed from the glovebox and concentrated under reduced pressure, and the yellow residue was purified by flash column chromatography (silica gel, 2.5% Et_3N, 2.5→40% EtOAc in hexanes, diam. 1.5 cm, ht. 18 cm) to give heptacyclic alcohol **9** (3.3 mg, 29%) hexacyclic alkene **10** (1.8 mg, 17%) as pale yellow oils.

Heptacyclic alcohol **9** underwent immediate and complete decomposition upon exposure to neutral alumina gel and partial decomposition upon extended exposure (>15 min) to triethylamine-neutralized silica gel. Hexacyclic alkene **10** also underwent partial decomposition upon extended exposure (>10 min) to triethylamine-neutralized silica gel. Separation of **9** and **10** was achieved by rapid elution of **10** (<1 min) followed by swift progressive increase in the polarity of the eluent (<10 min total for full elution of **9**).

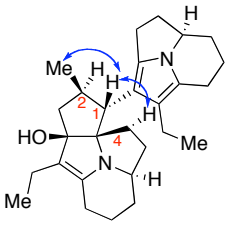
Data for heptacyclic alcohol **9**:

Best spectra were obtained by immediate use of samples and complete assignment was possible with the aid of additional information from gCOSY, gHSQC, gHMBC, and gNOESY.

^{1}H NMR (500 MHz, C_6D_6, 20 ˚C): 3.39 (tdd, J = 10.7, 5.1, 3.6 Hz, 1H, C4a'–H), 2.96 (ddd, J = 15.3, 11.1, 6.3 Hz, 1H, C3'–H_c), 2.75 (dd, J = 15.2, 7.8 Hz, 1H, C3'–H_t), 2.56–2.63 (m, 4H, C7'–H_c, C11'–H, C11'–H', C5a–H), 2.52 (d, J = 11.7 Hz, 1H, C1–H), 2.38–2.46 (m, 3H, C4–H_t, C7'–H_t, C3–H_c), 2.22–2.26 (m, 1H, C8–H_t), 2.06–2.19 (m, 4H, C11–H, C2–H, C11–H', C4'–H_c), 1.81 (td, J = 12.9, 4.4 Hz, 1H, C8–H_c), 1.54–1.76 (m, 6H, C6–H_c, C4–H_c, C6'–H_t, C4'–H_t, C5'–H_c, C3–H_t), 1.30–1.42 (m, 3H, C6–H_t, C7–H_c, C6'–H_c), 1.27 (t, J = 7.5 Hz, 3H, C12'–H), 1.18–1.27 (m, 2H, C5–H_t, C7–H_t), 1.13 (t, J = 7.6 Hz, 3H, C12–H), 0.98 (d, J = 6.5 Hz, 3H, C10'–H), 0.90–1.00 (m, 1H, C5–H_c), 0.89 (br q, J = 12.2 Hz, 1H, C5'–H_t).

[5] The corresponding C1 ketone was synthesized as a 1:1 mixture of C2 epimers; lithium aluminum hydride reduction produced **8** as an inseparable mixture of four diastereomers in a ratio of 5:9:5:8.

Select gNOESY data (500 MHz, C_6D_6, 20 ˚C):



^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 145.2 (C8a), 129.7 (C2a'), 123.3 (C1'), 117.4 (C7a'), 115.1 (C8b), 111.1 (C2'), 92.0 (C3a), 86.1 (C3b), 59.4 (C5a), 55.5 (C4a'), 55.0 (C1), 48.7 (C3), 37.5 (C4'), 35.3 (C2), 30.3 (C5'), 29.5 (C4), 28.4 (C3'), 28.4 (C5), 27.7 (C6), 24.8 (C8), 23.2 (C6'), 21.2 (C7'), 20.6 (C7), 19.1 (C11'), 18.4 (C10'), 18.1 (C11), 17.8 (C12), 17.4 (C12').

FTIR (thin film) cm^{-1}: 3455 (br m), 2952 (s), 1727 (m), 1673 (m), 1455 (s), 1025 (m).

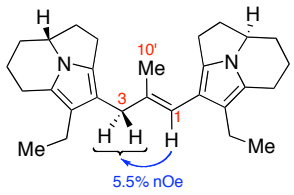
HRMS (ESI): calc'd for $C_{28}H_{41}N_2O$ $[M+H]^+$: 421.3213, found: 421.3216.

TLC (2.5% Et_3N in [2.5% EtOAc in hexanes], Et_3N neutralized silica gel), *Rf*: 0.25 (UV, CAM).

Data for hexacyclic alkene **10**:
Best spectra were obtained by immediate use of samples and complete assignment was possible with the aid of additional information from gCOSY, HSQC, and gHMBC.

^{1}H NMR (500 MHz, C_6D_6, 20 ˚C): 6.63 (s, 1H, C1–H), 3.66 (d, *J* = 15.2 Hz, 1H, C3–H), 3.52 (d, *J* = 15.2 Hz, 1H, C3–H'), 3.28–3.35 (m, 2H, C4a'–H, C5a–H), 2.50–2.75 (m, 9H, C4–H_c, C4–H_t, C11–H, C11–H', C11'–H, C11'–H', C7'–H_c, C8–H_c, C3'–H_c), 2.52 (dd, *J* = 14.7, 8.1 Hz, 1H, C3'–H_t), 2.36–2.47 (m, 2H, C7'–H_t, C8–H_t), 2.04 (s, 3H, C10'–H), 2.01 (dt, *J* = 11.7, 6.0 Hz, 1H, C5–H_c), 1.94 (dt, *J* = 11.4, 5.7, 1H, C4'–H_c), 1.56–1.71 (m, 3H, C6'–H_t, C7–H_t, C5–H_t), 1.46–1.56 (m, 3H, C5'–H_c, C6–H_c, C4'–H_t), 1.25–1.42 (m, 2H, C6'–H_c, C7–H_c), 1.35 (t, *J* = 7.5 Hz, 3H, C12–H *or* C12'–H), 1.33 (t, *J* = 7.5 Hz, 3H, C12–H *or* C12'–H), 0.87 (br q, *J* = 12.2 Hz, 1H, C5'–H_t *or* C6–H_t), 0.81 (br q, *J* = 12.2 Hz, 1H, C5'–H_t *or* C6–H_t).

nOe data (500 MHz, C_6D_6, 20 ˚C):



^{13}C NMR (125 MHz, C_6D_6, 20 ˚C): 134.2 (C2), 128.9 (C2a'), 128.8 (C3b), 122.2 (C8b *or* C1'), 122.2 (C8b *or* C1'), 119.4 (C1), 119.0 (C8a), 118.5

(C7a'), 114.1 (C2'), 112.5 (C3a), 55.5 (C4a'), 55.4 (C5a), 37.8 (C4'), 37.7 (C5), 37.3 (C3), 30.5 (C5' *or* C6), 30.5 (C5' *or* C6), 27.6 (C3'), 25.3 (C4), 23.3 (C6' *or* C7), 23.0 (C6' *or* C7), 21.2 (C7' *or* C8), 21.0 (C7' *or* C8), 19.5 (C11 *or* C11'), 19.3 (C11 *or* C11'), 19.0 (C10'), 16.9 (C12 *or* C12'), 16.8 (C12 *or* C12').

FTIR (thin film) cm^{-1}: 2926 (s), 1651 (m), 1455 (m), 1088 (w), 736 (w).

HRMS (ESI): calc'd for $C_{28}H_{39}N_2$ $[M+H]^+$: 403.3108,
found: 403.3107.

TLC (2.5% Et_3N in [2.5% EtOAc in hexanes], Et_3N neutralized silica gel), *Rf*: 0.54 (UV, CAM).

ACQUISITION	
sfrq	499.745
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fb	not used
bs	1
tpwr	56
pw	8.6
d1	1.000
tof	263.4
nt	10000
ct	10
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-249.9
wp	6246.8
vs	164
sc	0
wc	250
hzmm	24.99
is	161.11
rfl	681.3
rfp	0
th	32
ins	1.000
ai cdc ph	

DEC. & VT	
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dn	C13
dpwr	30
dof	0
dm	nnn
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
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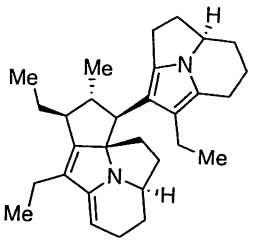
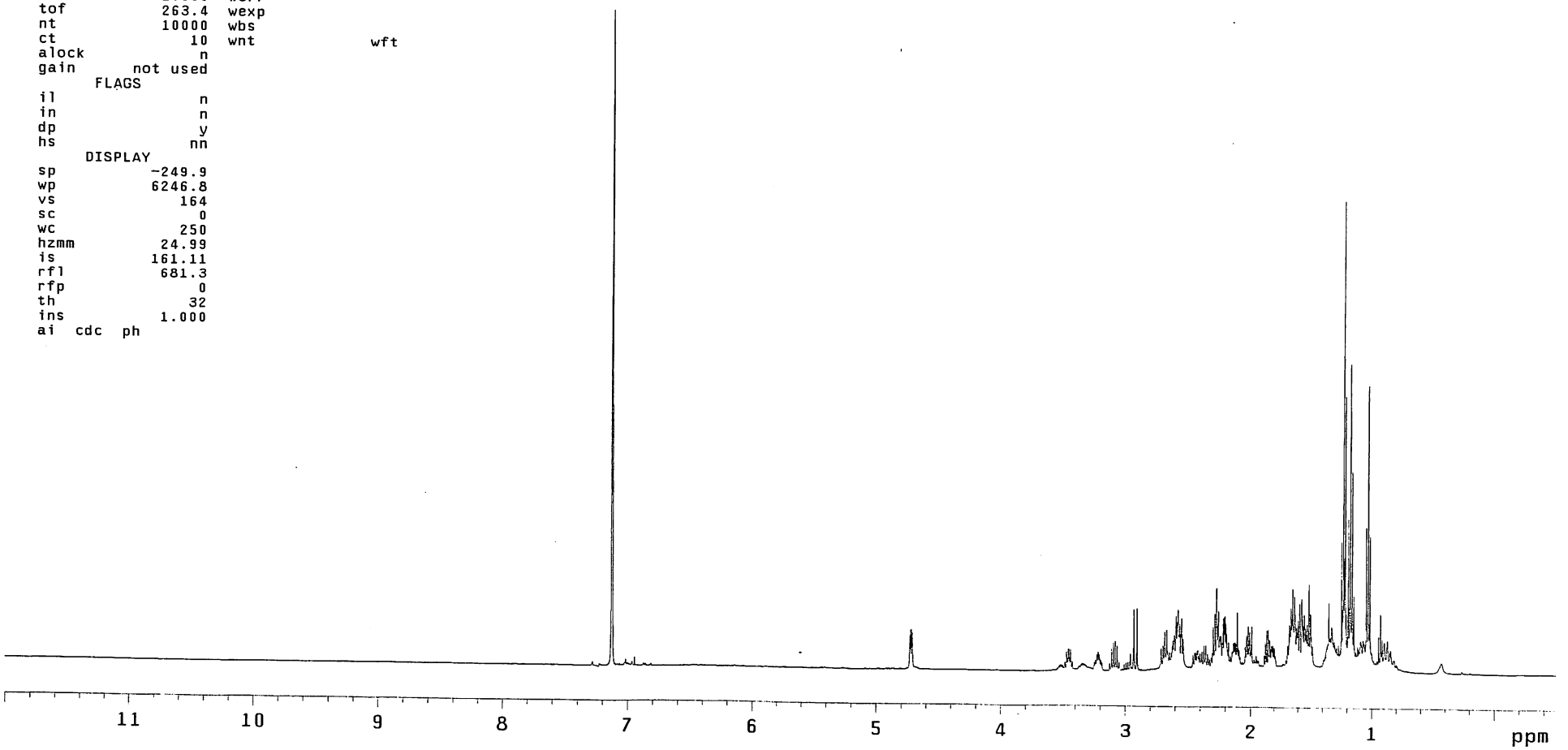
proc	ft
fn	262144
math	f
werr	
wexp	
wbs	
wnt	wft



isoM430B



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fb	not used	dmm	w
bs	8	dmf	10000
ss	1	dseq	
tpwr	54	dres	1.0
pw	6.9	homo	n
d1	0.763	PROCESSING	
tof	1027.4	lb	1.00
nt	1e+06	wtfile	
ct	848	proc	ft
alock	n	fn	131072
gain	not used	math	f
FLAGS			
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	
DISPLAY			
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wp	28303.6		
vs	866		
sc	0		
wc	250		
hzmm	113.21		
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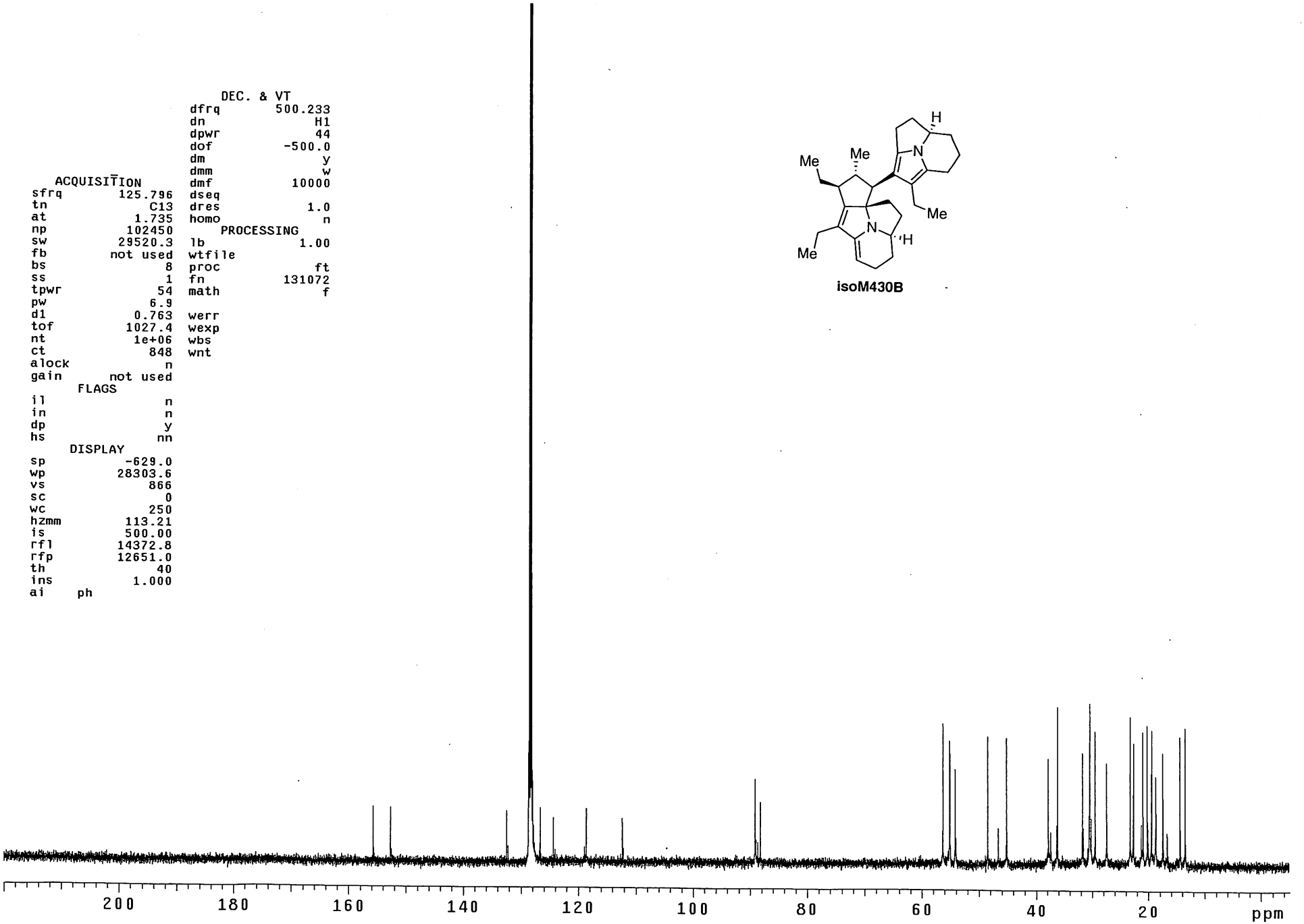
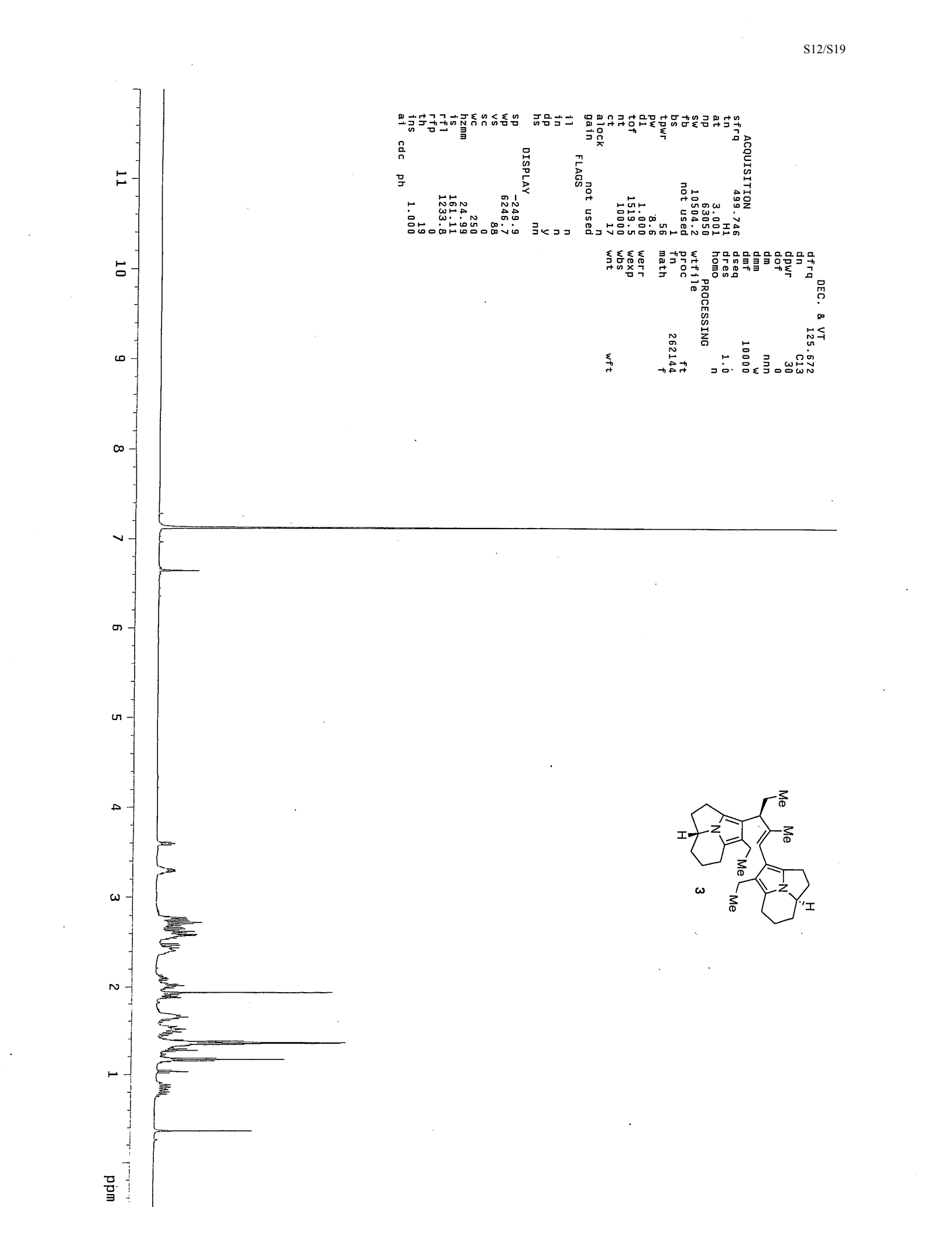
ins	1.000		
ai	ph		

isoM430B

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dres 1.0
homo n
PROCESSING
wtfile
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fn 262144
math f
wft
wnt
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sfrq 499.746
tn H1
at 3.001
np 63050
sw 10504.2
fb not used
bs 1
tpwr 56
pw 8.6
d1 1.000
tof 1519.5
nt 10000
ct 17
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 6246.7
vs 88
sc 0
wc 250
hzmm 24.99
is 161.11
rfl 1233.8
rfp 0
th 19
ins 1.000
ai cdc ph
Me
Me
Me
Me
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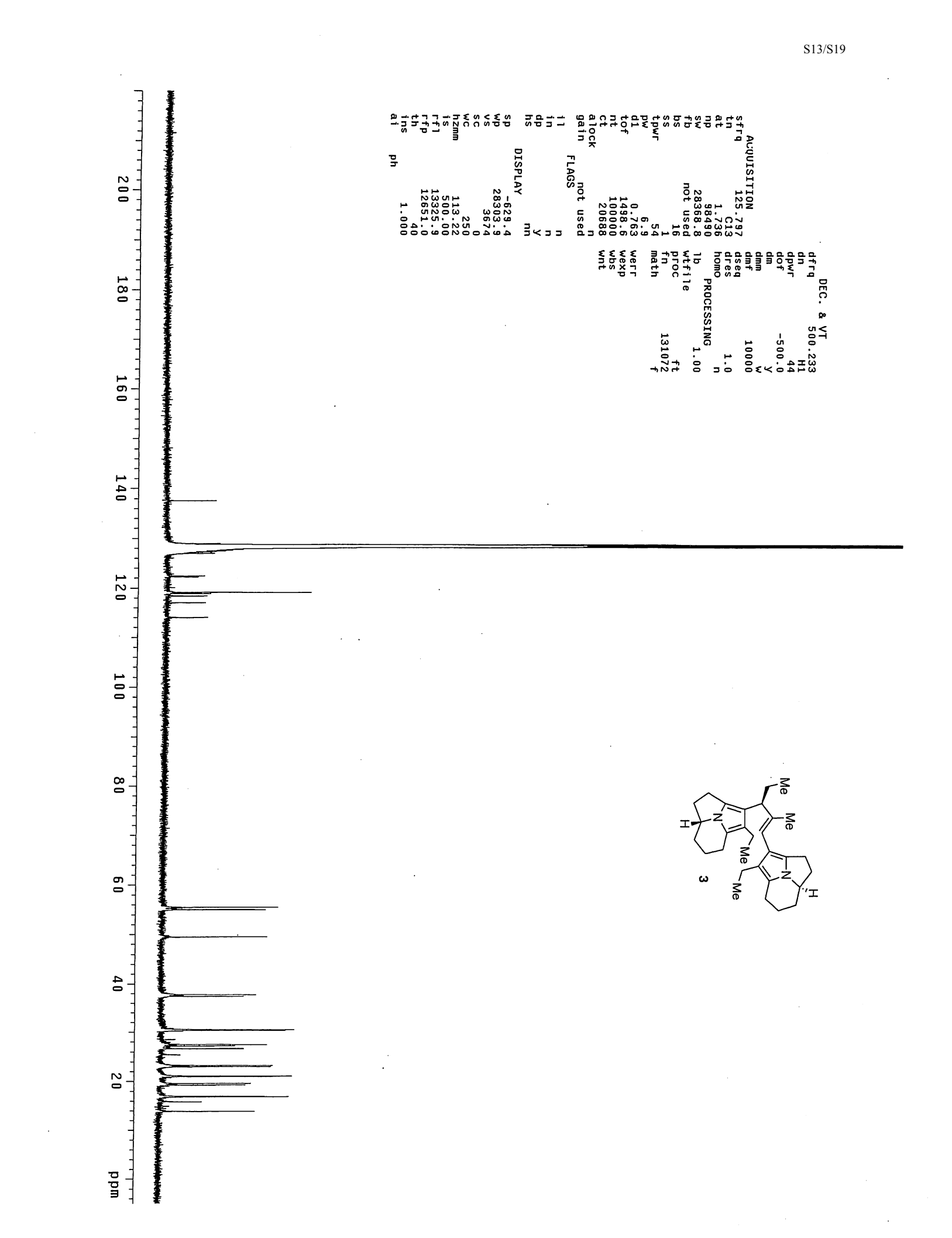
N
H
H
3
11
10
9
8
7
6
5
4
3
2
1
ppm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dmm w
dmf 10000
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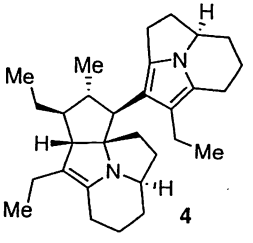
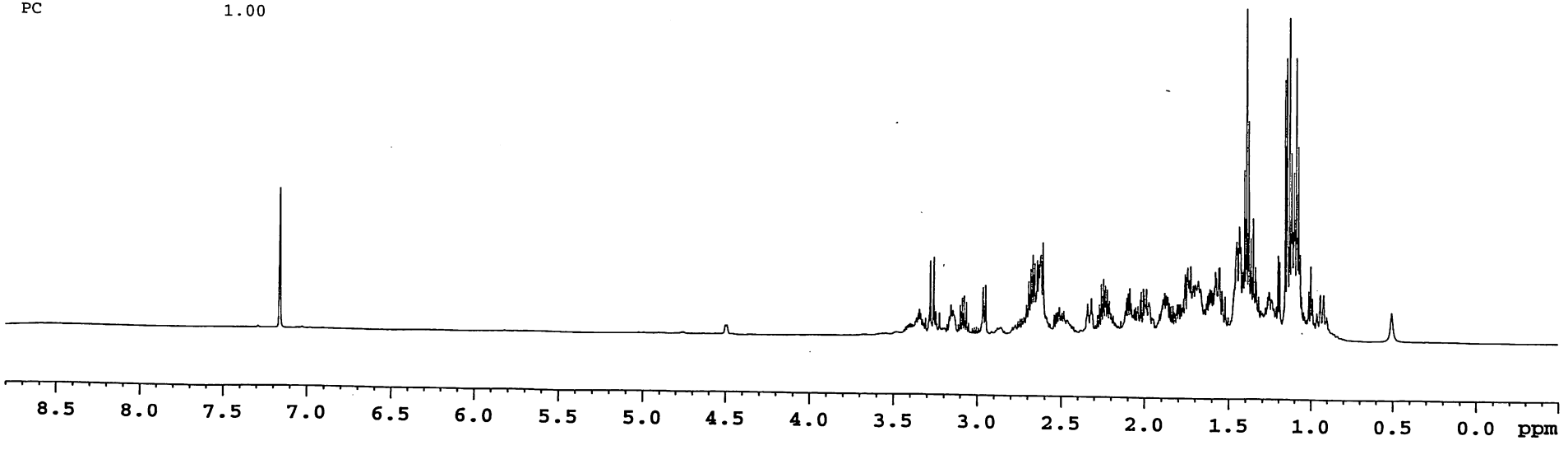
at 1.736
np 98490
sw 28368.8
fb not used
bs 16
ss 1
tpwr 54
pw 6.9
d1 0.763
tof 1498.6
nt 100000
ct 20688
alock n
gain not used
PROCESSING
lb 1.00
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -629.4
wp 28303.9
vs 3674
sc 0
wc 250
hzmm 113.22
is 500.00
rfl 13325.9
rfp 12651.0
th 40
ins 1.000
ai ph
Me
Me
N
H
Me
Me
N
H
3
200
180
160
140
120
100
80
60
40
20
ppm

F2 - Acquisition Parameters

INSTRUM	spect
PROBHD	5 mm CPTXI Z-G
PULPROG	zg
TD	32768
SOLVENT	C6D6
NS	8
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	16
DW	83.200 usec
DE	6.00 usec
TE	293.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	8.15 usec
PL1	-6.00 dB
SFO1	600.4674019 MHz
F2 - Processing parameters	
SI	65536
SF	600.4650662 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



4



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sw	29411.8
fb	not used
bs	8
ss	1
tpwr	54
pw	6.9
d1	0.763
tof	1870.6
nt	100000
ct	2080
alock	n
gain	not used

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-629.2
wp	28303.7
vs	1030
sc	0
wc	250
hzmm	113.21
is	500.00
rfl	13475.4
rfp	12651.0
th	25
ins	1.000
nm	ph

DEC. & VT	
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dn	H1
dpwr	44
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n

PROCESSING	
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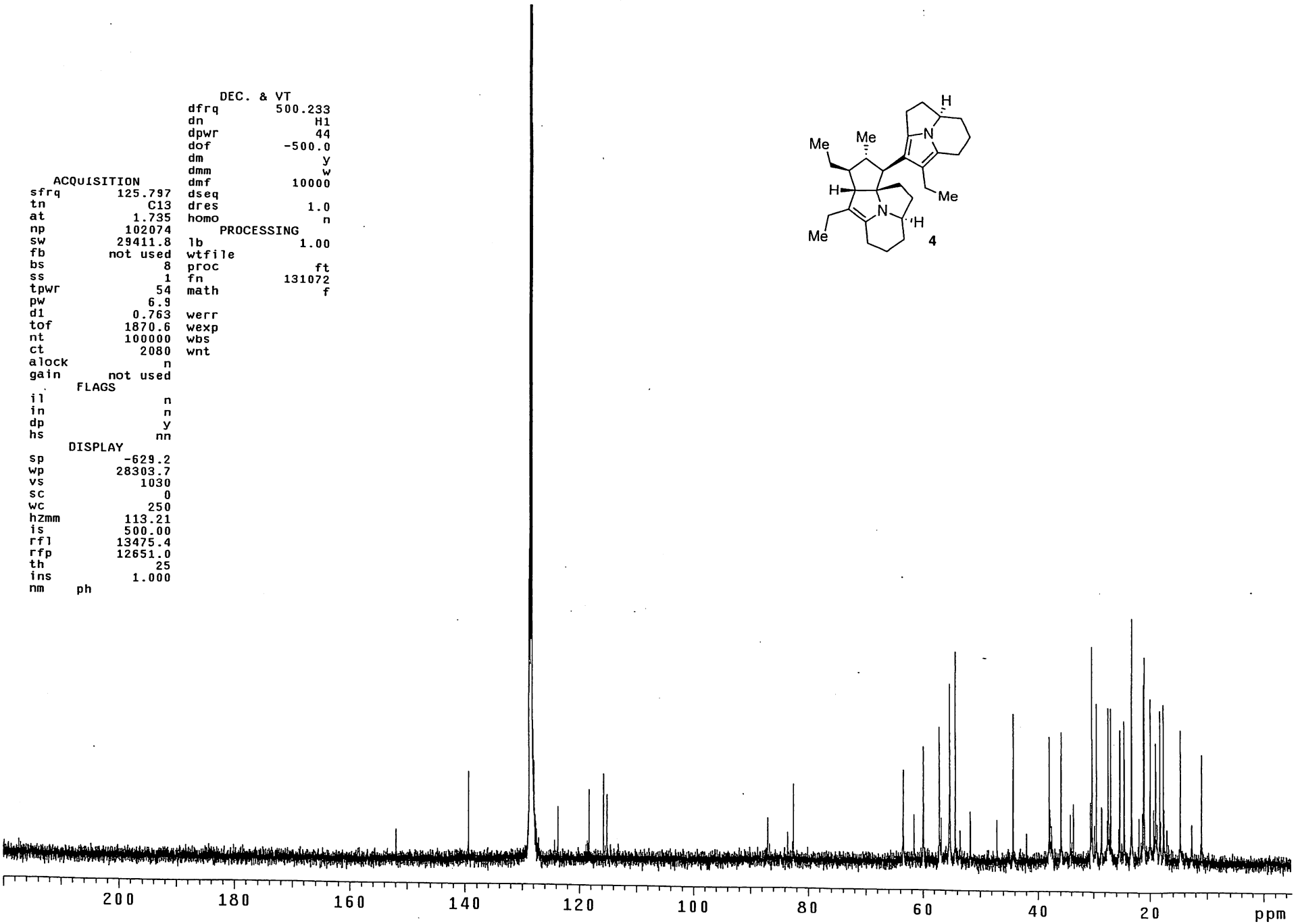
proc	ft
fn	131072
math	f
werr	
wexp	
wbs	
wnt	

4



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np	63050	dof	0
sw	10504.2	dm	nnn
fb	not used	dmm	w
bs	1	dmf	10000
tpwr	56	dseq	
pw	8.6	dres	1.0
d1	1.000	homo	n
tof	1519.5	temp	20.0
nt	1000	PROCESSING	
ct	26	wtfile	
alock	n	proc	ft
gain	not used	fn	262144
FLAGS		math	f
il	n	werr	
in	n	wexp	
dp	y	wbs	
hs	nn	wnt	wft
DISPLAY			
sp	-249.9		
wp	6246.7		
vs	152		
sc	0		
wc	250		
hzmm	24.99		
is	33.57		
rfl	1233.8		
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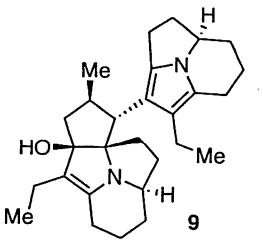
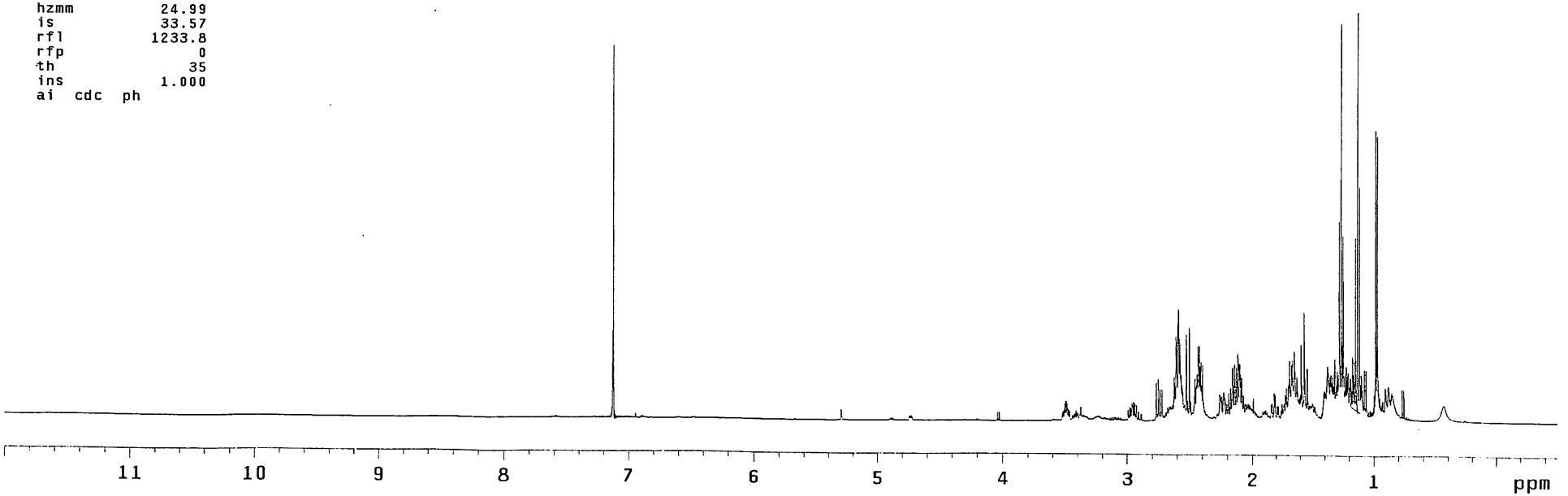
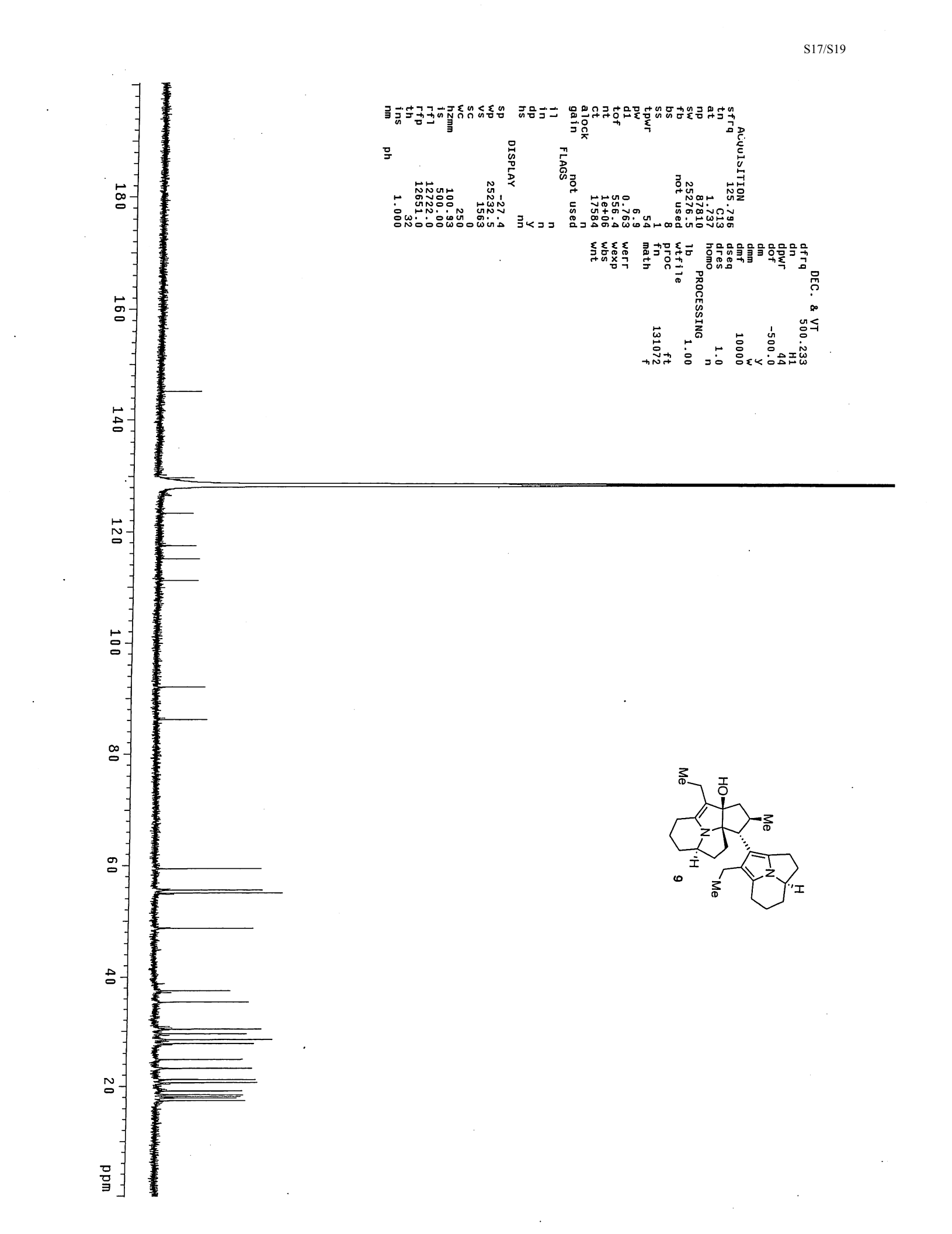
ins	1.000		
ai cdc ph			



9

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dmm w
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at 1.737 homo n
np 87810 PROCESSING
sw 25276.5 lb 1.00
fb not used wtfile
bs 8 proc
ss 1 ft
tpwr 54 fn 131072
pw 6.9 math f
d1 0.763 werr
tof 556.4 wexp
nt 1e+06 wbs
ct 17584 wnt
alock n
gain FLAGS
not used
il n
in n
dp y
hs nn
DISPLAY
sp -27.4
wp 25232.5
vs 1563
sc 0
wc 250
hzmm 100.93
is 500.00
rfl 12722.0
rfp 12651.0
th 32
ins 1.000
nm ph
HO
Me
N
H
Me
N
H
Me
9
180
160
140
120
100
80
60
40
20
ppm

ACQUISITION	
sfrq	499.746
tn	H1
at	3.001
np	63050
sw	10504.2
fb	not used
bs	1
tpwr	56
pw	8.6
d1	1.000
tof	1519.5
nt	1000
ct	33
alock	n
gain	not used
FLAGS	
il	n
in	n
dp	y
hs	nn
DISPLAY	
sp	-249.9
wp	6246.7
vs	48
sc	0
wc	250
hzmm	24.99
is	33.57
rfl	1233.8
rfp	0
th	22
ins	1.000
ai cdc ph	

DEC. & VT	
ifrq	125.672
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dpwr	30
dof	0
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dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
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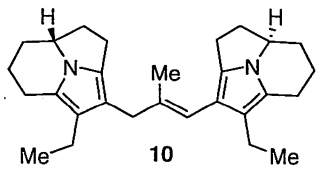

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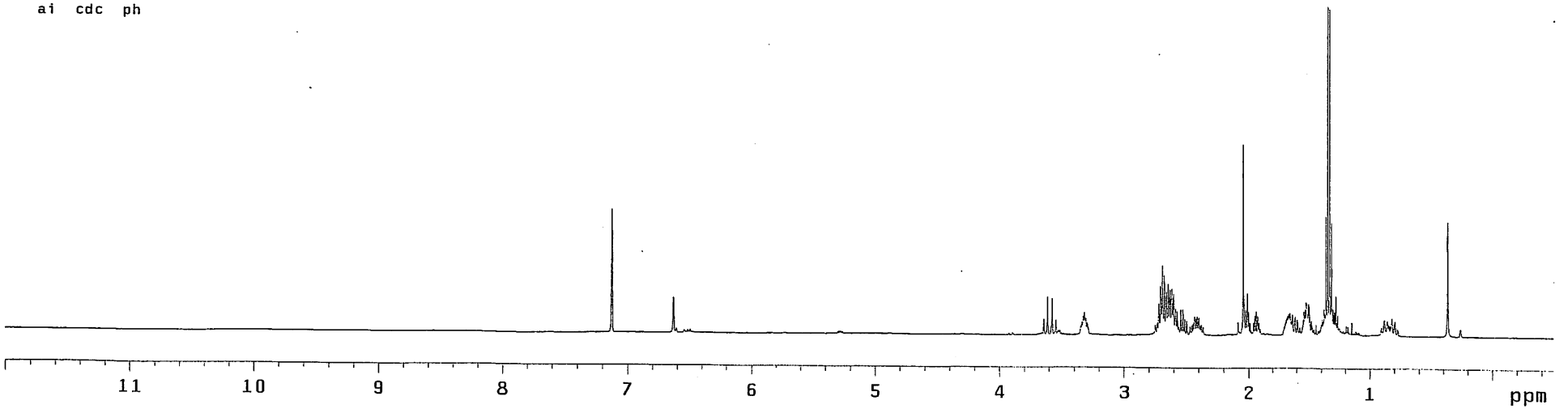

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ss	1
tpwr	54
pw	6.9
d1	0.763
tof	-806.7
nt	1e+09
ct	14992
alock	n
gain	60
FLAGS	
il	n
in	n
dp	y
hs	nn
DISPLAY	
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wp	23705.4
vs	3215
sc	0
wc	250
hzmm	94.82
is	500.00
rfl	13330.3
rfp	12651.0
th	39
ins	1.000
nm	ph

DEC. & VT	
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dpwr	44
dof	-500.0
dm	y
dmm	w
dmf	10000
dseq	
dres	1.0
homo	n
PROCESSING	
lb	1.00
wtfile	
proc	ft
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math	f
werr	
wexp	
wbs	
wnt	

10